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### Specifications

#### 1. Title of the Invention

Method for Detoxification of Nitrogen Trifluoride

#### 2. Limits of the Patent Claims

(Claim 1) A method for detoxification of nitrogen trifluoride; the method comprising the steps of: mixing together of nitrogen trifluoride-containing gas and steam (water vapor); and decomposition by causing the nitrogen trifluoride to react with water.

(Claim 2) A method for detoxification of nitrogen trifluoride as in Claim 1; wherein nitrogen trifluoride and water are reacted in the gas phase at a temperature of at least 300 °C.

#### 3. Detailed Explanation of the Invention

The present invention relates to a method for detoxification of nitrogen trifluoride.

#### [Prior Art]

Gaseous inorganic nitrogen compounds have come to be used in recent years as dry etching gases or as CVD raw material gases. Such nitrogen compounds include nitrogen trifluoride, tungsten hexafluoride, sulfur hexafluoride, and the like.

Among such inorganic nitrogen compounds, nitrogen trifluoride has received particular attention for the following reasons. Nitrogen trifluoride forms a plasma at a lower discharge

energy than Freon 14, etc. since bond energy of the  $\text{NF}_2\text{-F}$  bond is roughly one half that of the  $\text{CF}_3\text{-F}$  bond, thereby widening the temperature range of dry etching. Furthermore, carbon contamination of the wafer surface does not occur since the nitrogen trifluoride molecule does not contain carbon. [TRANSLATOR'S NOTE: Legibility of subscripts in chemical formulae throughout the document was very poor. Some of these may have been translated incorrectly.]

Moreover, attention has recently been paid to nitrogen trifluoride as a chamber cleaning gas for CVD equipment, particularly as a cleaning gas for cleaning by plasma etching removal of tungsten, tungsten silicide, silicon oxide, polysilicon, etc. from the chamber interior. It is thought that demand for such applications will increase.

#### [Problems to be Solved by the Invention]

Nitrogen trifluoride has a toxicity that resembles that of carbon monoxide. The TWA value (permissible concentration in a 8 hour per day work environment, 40 work hours per week) is 10 ppm. Residual nitrogen trifluoride in exhaust gas must be reduced at least below 10 ppm.

Since nitrogen trifluoride is a stable chemical compound that is nearly non-reactive with acidic or basic aqueous solutions at temperatures below 100 °C, a previously considered treatment method has been a decomposition treatment comprising mixture with a flammable gas (such as methane), followed by combustion of the gas mixture. However, this method can not be said to be advantageous from the standpoints of cost and operability since complete decomposition of nitrogen trifluoride by this method is difficult.

Other nitrogen trifluoride treatment methods that have been reported include: reaction of nitrogen trifluoride with Si, B, W, Mo, V, Se, Te, Ge, and non-volatile oxides thereof (Publication of Examined Patent Application No. Sho 63-48570); reaction with carbon (Publication of Unexamined Patent Application No. Sho 62-237929), and the like. Increasing treatment efficiency by modification of reaction conditions during these methods is difficult. Furthermore, there is the possibility of forming toxic substances (such as  $\text{COF}_2$ , etc.) as reaction byproducts.

#### [Means to Solve the Problems]

The goal of the present invention is to solve the above mentioned problems so as to provide an efficient, simple, and safe method for detoxification treatment of nitrogen trifluoride-containing gas while also avoiding atmospheric contamination and work place environmental problems.

Specifically, the present invention is a method for detoxification of nitrogen trifluoride; the method comprising the steps of: mixing together of nitrogen trifluoride-containing gas and steam (water vapor); and decomposition by causing the nitrogen trifluoride to react with water.

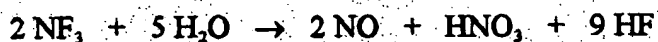
The preferred temperature for reacting nitrogen trifluoride with hydrogen chloride is at least 300 °C. Reaction temperatures below 300 °C are undesirable due to concern that the reaction might not proceed sufficiently. Although increased temperature is advantageous for facilitating the reaction, equipment becomes more complex and reactant handling becomes more difficult as temperature rises. Therefore a reaction temperature below 1000 °C is preferred, or more preferably 300 to 700 °C. [TRANSLATOR'S NOTE: Mention of "hydrogen chloride" in the source text is an apparent error.]

Specifically, the method of the present invention is preferably carried out in the manner described below. First, nitrogen trifluoride-containing gas is mixed with steam (water vapor).

Distilled water is preferably used for generation of this steam in order to prevent contamination of the steam generation equipment. It is permissible for this steam to contain inert gas, etc. The mixed gas is fed to the reactor and is made to undergo a gas phase reaction. The nitrogen trifluoride and steam may be mixed within the reactor itself.

No particular limitations are placed upon the reactor. A preferred reactor type is a cylindrical vessel equipped with a heating device that surrounds the reactor. Residence time of the mixed gas within this reactor is preferably 10 to 60 seconds. When this residence time is less than 10 seconds, there is concern that the reaction might not proceed sufficiently. On the other hand, a residence time in excess of 60 seconds is undesirable due to concern that the reactor equipment would become unnecessarily large.

The reaction between nitrogen trifluoride and water is thought to proceed as indicated by the equation below.



[TRANSLATOR'S NOTE: This reaction is not balanced, apparently an error in the source text. This should probably read " $3 \text{NF}_3 + 5 \text{H}_2\text{O} \rightarrow 2 \text{NO} + \text{HNO}_3 + 9 \text{HF}$ ."]

Among the above mentioned reaction products,  $\text{HNO}_3$  and  $\text{HF}$  can be readily removed by known methods, such as alkaline scrubbing and the like. After oxidation by  $\text{O}_2$ , etc.,  $\text{NO}$  can be easily removed in the same manner by alkaline scrubbing and the like. Furthermore, all of these reaction products are either gases or liquids. Therefore blockage of the reactor by solids is not a problem.

The quantity of steam mixed together with the nitrogen trifluoride-containing gas is preferably in excess of that required by stoichiometry as indicated by the above mentioned equation.

The nitrogen trifluoride-containing gas of the present invention may be pure nitrogen trifluoride gas or nitrogen trifluoride mixed with another gas. There are no particular limitations placed upon the co-existing gas. Examples of the co-existing gas that may be used include inert gases (nitrogen, argon, helium, etc.), other dry etching gases (Freons, chlorides, etc.), oxygen, chlorine, hydrogen fluoride, etc.

#### [Working Example]

Within a CVD apparatus, a tungsten silicide film was formed upon a silicon wafer using a mixed gas comprising monosilane and tungsten hexafluoride. Then nitrogen trifluoride (better than 99.9% purity) was fed at a rate of 200 ml per minute, and tungsten silicide deposited upon the CVD apparatus chamber interior wall was removed by plasma etching. The exhaust gas vented from the chamber contained roughly 2% nitrogen trifluoride.

This exhaust gas (200 ml per minute) was mixed with steam (50 ml per minute), and the gas mixture was fed through a tubular reactor that was 27 mm internal diameter and 300 mm long. This tubular reactor was maintained at 600 °C by an external heater. After the tubular reactor, nitrogen trifluoride content of the exhaust gas was examined by gas chromatographic analysis. Nitrogen trifluoride was below the detection limit (1 ppm). This analytical result remained unchanged even after 30 minutes of continuous exhaust gas feed.

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**[Results of the Invention]**

By use of the method of the present invention, nitrogen trifluoride can be readily removed at high efficiency from a nitrogen trifluoride-containing gas, and nitrogen trifluoride can be detoxified. Furthermore, the method of the present invention can be safely carried out without producing a gas that is flammable or toxic, etc.

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